

PATENT SPECIFICATION

NO DRAWINGS

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822.621

Date of filing Complete Specification: Aug. 7, 1957.

Application Date: Sept. 5, 1956.

No. 27133/56.

Complete Specification Published: Oct. 28, 1959.

Index at acceptance:—Classes 2(6), P2(C13A: C13C: C20B: D1A: D1B: D2A: K2: K7: K8: T2A); and 70, Q5B.

International Classification:—C08c, d.

COMPLETE SPECIFICATION

Vulcanisable Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to vulcanisable compositions.

Isotactic polypropylene is a crystalline material suitable for moulding and extrusion having a melting point of approximately 160° C. We have found that despite this high melting point it can be mixed with natural or synthetic rubber by a masticating process. We have also found that the presence of isotactic polypropylene is vulcanised natural or synthetic rubber compositions results in reinforcement to a remarkable extent.

According to the present invention, therefore, we provide vulcanisable compositions containing a major proportion of natural and/or synthetic rubber and a lesser proportion of isotactic polypropylene. We also provide a method for the production of these compositions in which method isotactic polypropylene is dispersed in the rubber by a hot masticating treatment in the absence of vulcanising ingredients and the mixture obtained is cooled and vulcanising ingredients are dispersed in it by mastication at a lower temperature.

Synthetic rubbers which may be used in this invention include copolymers of butadiene and styrene or acrylonitrile, copolymers of isoprene and isobutylene and polymers and copolymers of chloroprene.

Our preferred quantities of isotactic polypropylene in the compositions of this invention are between 1 and 40%, preferably between 5 and 25% by weight of the combined weight of rubber and isotactic polypropylene, very useful compositions being obtained with

mixtures with natural rubber containing between 6 and 20% isotactic polypropylene.

By isotactic polypropylene we mean any solid polymer of propylene which contains a major proportion of crystalline polypropylene and preferably is at least 70% by weight insoluble in hot heptane. Also isotactic polypropylene may contain minor quantities as impurity or atactic polypropylene, i.e. polypropylene having a random steric distribution of methyl side groups along the greater part of its polymer chain and therefore not being crystallisable in itself. As a result, isotactic polypropylene normally melts over a range of temperatures. For ease of dispersion with rubber we prefer that the isotactic polypropylene used in the compositions and process of our invention has a melt viscosity at 190°C. less than 10⁷ poises when measured with a parallel plate plastometer at a shear rate of 0.1 per second. Isotactic polypropylenes having melt viscosities between 10⁴ and 10⁵ poises at 190°C. result in a combination of particular ease in the operation of the process of our invention and the production of particularly useful compositions.

We prefer that in the preparation of the compositions of this invention rubber is masticated with isotactic polypropylene in the absence of vulcanising ingredients at a temperature between 150°C. and the maximum of the isotactic polypropylene melting point range. Thus particularly suitable temperatures are from 150°C. to 170°C. depending upon the melting point of the polypropylene. For ease of dispersion, the polypropylene is preferably supplied for mastication in the form of fine powder. Mastication may be accomplished in, for example, a Banbury mixer or on open roll mills. In the former case, it is best to supply a dry blend of the ingredients to the mixer in order to minimise the mixing time and to complete the mixing on rolls in

[Price

order to convert the mix to the form of sheet and thereby facilitate its cooling. If mastication is conducted on rolls only, a very satisfactory method is to sheet the rubber on the rolls, add powdered isotactic polypropylene and continue milling until the polypropylene is dispersed. Dispersion of the polypropylene in natural rubber is indicated by translucency in the mixture when hot.

This mastication of rubber and polypropylene is preferably conducted in the presence of an antioxidant. Suitable antioxidants are bis-(2 hydroxy - 3 - t - butyl - 5 - methylphenyl) methane, bis - (2 hydroxy - 3 - alpha - methylcyclohexyl-5-methyl phenyl) methane, a mixture resulting from condensing 2,4 and 2,5 dimethyl phenol with butyraldehyde and phenyl beta naphthylamine. Suitable quantities of antioxidant are between 0.5% and 2.0% by weight of the composition. Commercial synthetic rubbers often contain such quantities of antioxidants.

Particularly suitable temperatures for masticating the rubber/polypropylene mix with vulcanising ingredients are between 60 and 80°C. for natural rubber and 25—50°C. for synthetic rubber. Again suitable equipment are Banbury mixers (preferably followed by open roll mills for sheeting) or open roll mills. Ancillary ingredients, for example, fillers and pigments, may usefully be added to the compositions together with the vulcanising ingredients.

Particularly valuable properties which are obtained when the compositions of our invention are vulcanised are those of low density, high tensile strength, high modulus of elasticity, high resilience, high hardness, high tear and abrasion resistance and excellent electrical properties, with a remarkable retention of these good properties at elevated temperatures, all without the necessity of including dark coloured fillers. The compositions are accordingly particularly suitable for the production of light coloured articles of low heat build up, or light coloured articles in which a high degree of reinforcement is maintained at elevated temperatures or for use in applications where a high tear strength and abrasion resistance is required. Fillers such as carbon black

may be incorporated in the compositions if desired. Such compositions can combine good reinforcement with high resiliences and low heat build up.

The following Examples, in which all parts are by weight, serve to illustrate our invention. It will be understood, however, that our invention is in no way limited by these Examples. In Examples 5—18 the rubbers used contained anti-oxidants.

EXAMPLE 1

160 gms. natural rubber were sheeted on a 12" x 6" open roll mill with 2 gms. bis-(2 hydroxy-3-t-butyl-5-methyl phenyl) methane at 155—160°C. and 40 gms. powdered polypropylene were added. This polypropylene had a melt viscosity at 190°C. of 5.6×10^4 poises measured on a parallel plate plastometer under a shear rate of 0.1 per second. When tested for solubility in heptane by Soxhlet extraction, 75% by weight of it was found to be insoluble. 10 minutes after all the polypropylene had been added the sheet became translucent and was removed from the mill and cooled.

The sheet obtained was fed to a 12" x 6" open roll mill heated to 60°C. and the following ingredients were added:

1.2 gms. cyclohexyl benzthiazyl sulphenamide
10.0 gms. zinc oxide
4.0 gms. stearic acid
5.0 gms. sulphur

The mixture was milled for 15 minutes during which time the temperature of the roll carrying the sheet was allowed to rise to 80°C. The sheet was cooled and test mouldings were moulded from it with a cure time of 30 minutes at 140°C. under a pressure of 1,000 lb./sq. inch.

The properties of the mouldings were:

Tensile strength 3,150 lb./sq. in.
Elongation at Break 500%
Stress at 100% strain 990 lb./sq. in.
Stress at 300% strain 1,910 lb./sq. in.

(The above tests were conducted according to B.S. 903 (1950) using ring specimens).

Hardness, B.S. 903 (1950)

80 BS°

Crescent tear strength, B.S. 903 (1950)

1,2000 lb./sq. in.

Resilience (Dunlop
Tripsometer—
B.S. 903 (1950))

at 20° C. 59%
at 50°C 67%
at 70° C. 69%

Dynamic Young's Modulus

at 0°C. 2.78×10^8 dynes cm²
at 30°C. 1.7×10^8 " "
at 60°C. 1.25×10^8 " "
at 80°C. 1.15×10^8 " "
at 100°C. 1.0×10^8 " "

EXAMPLES 2, 3 and 4

100 parts natural rubber (ribbed, smoked sheet) were sheeted on open roll mills both rollers of which were heated to 150°C. the time of milling being 5 minutes. In Examples 2, 3 and 4, 10, 20 and 30 parts respectively of powdered polypropylene were added as soon as the rubber had been sheeted. This polypropylene had a melt viscosity at 190°C. of 5×10^4 poises measured on a parallel plate plastometer under a shear rate of 0.1 per second. When tested for solubility in heptane by Soxhlet extraction 95% by weight of it was found to be insoluble. The compounded sheet obtained was fed to an open roll mill heated to 60°C. and the following ingredients were added:

5 parts zinc oxide
2 parts steric acid
2 parts bis-(2 hydroxy-3-alpha-methyl-cyclohexyl-5-methyl phenyl) methane
2.5 parts sulphur
0.6 parts cyclohexyl benzothiazyl sulphenamide

25 The mixture was milled for 15 minutes, the sheet obtained was cooled and teste mouldings were obtained from it using cures of 30 minutes at 140°C. under a pressure of 1,000 lb./sq. in. The mouldings were tested according to B.S. 903 (1950) using ring specimens with results as shown in Table I.

15 sheet obtained was fed to an open roll mill heated to 60°C. and the following ingredients were added:

TABLE I

Example	Parts polypropylene per 100 parts rubber	Hardness °BS	Elongation at break %	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Tension Set % After 15 sec.	Tension Set % After 1 hr.	Resilience %
—	0	46	675	120	260	2550	5	0	88
2	10	61	620	320	780	3120	15	10	78
3	20	76	495	830	1860	3230	40	30	65
4	30	75	415	620	1050	1660	35	25	67.5

* Tension Set was measured 15 secs. and 1 hour after release from a strain of 300% maintained for 1 hour.

EXAMPLES 5, 6 and 7

The procedure of Examples 2, 3 and 4 was repeated replacing natural rubber by a butyl rubber sold commercially under the Registered Trade Mark "Butyl 200" by the Polymer Corporation of Sarnia.*

*"Butyl 200" is an isobutylene-isoprene copolymer having 1.4 mole % proportion of residual unsaturation, the residual unsaturation indicating the proportion of isoprene in the copolymer.

The vulcanisation ingredients were:

5 parts zinc oxide
2 parts sulphur
1 part tetramethyl thuramdisulphide
1 part zinc diethyl dithiocarbamate

These ingredients were milled with the rubber/polypropylene blend using rolls initially at 30°C. The test mouldings were cured for 20 minutes at 144°C. The test results were as shown in Table II.

TABLE II

Example	Parts polypropylene per 100 parts rubber	Hardness °BS	Elongation at break %	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Tension % after 15 sec.	Set * 1 hr.	Resilience %
—	—	30.5	905	60	100	1700	10	5	26
5	10	46	545	150	480	940	15	5	26.8
6	20	64	366	420	940	1080	35	20	25.5
7	30	66	200	420	—	660	—	—	25

* Measured as described for Table I

EXAMPLES 8, 9 AND 10

The procedure of Examples 2, 3 and 4 was repeated using a butadiene/styrene copolymer rubber sold commercially under the Registered Trade Mark "Krylene" NS by the Polymer Corporation of Sarnia*

*Krylene N.S. is a butadiene-styrene copolymer containing 75% butadiene and 25% styrene.

5 parts zinc oxide
2 parts stearic acid
2 parts sulphur

0.44 parts diphenyl guanidine
1.31 parts dibenzthiazyl disulphide

The rolls for milling these ingredients with the rubber/polypropylene mixture were initially at 30°C. Mouldings from the compositions obtained were cured for 40 minutes at 140°C. The test results on these mouldings are set out in Table III.

The vulcanisation ingredients were:

TABLE III

Example	Parts polypropylene per 100 parts rubber	Hardness °BS	Elongation at break %	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Resilience %
—	0	49.5	350	120	220	240	72
8	10	60.5	370	230	420	480	64.8
9	20	79	195	760	—	1000	56.3
10	30	86	100	1020	—	1020	43

EXAMPLES 11, 12, 13 and 14
 Natural rubber (ribbed, smoked sheet) was compounded as for Examples 2, 3 and 4 with various concentrations of carbon black (as sold under the Registered Trade Mark "Ukarb")

327) and various concentrations of polypropylene. The milled sheets were cooled, compounded with vulcanisation ingredients, cured and tested as in the previous Examples. The results of the tests are as set out in Table IV.

TABLE IV

Example	Parts carbon per 100 parts rubber	Parts polypropylene per 100 parts rubber	Hardness °BS	Elongation at break %	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Tension Set % after 15 sec.	Tension Set * 1 hr.	Resilience %
—	50	0	65	440	360	1760	2860	20	15	67.5
11	40	5	66	495	350	1520	3000	18	12	68
12	30	10	70	495	420	1420	2880	26	10	65
13	20	15	72	535	500	1360	3120	20	15	66
14	10	20	72	540	540	1400	3120	40	25	66

* Measured as described for Table I

EXAMPLES 15, 16, 17 and 18
 Butyl rubber as sold under the Registered
 Trade Mark "Butyl 200" was compounded
 as for Examples 2, 3 and 4 with various con-
 centrations of carbon black (as sold under the
 name "Ukarb" 327) and various concentra-

tions of polypropylene. The milled sheets
 were cooled, compounded with vulcanisation
 ingredients, cured and tested as in the previous
 Examples. The results of the tests are as set
 out in Table V.

TABLE V

Example	Parts carbon per 100 parts rubber	Parts polypropylene per 100 parts rubber	Hardness °BS	Elongation at break %	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Tension % after 15 sec.	Set * 1 hr.	Resilience %
—	50	0	55	700	160	520	1650	10	5	20.8
15	40	5	52.5	755	160	450	1900	15	10	21
16	30	10	53	740	180	500	1990	10	5	26.5
17	20	15	54	645	250	640	1850	15	10	26.3
18	10	20	56	615	260	650	1660	15	10	27.5

* Measured as described for Table I

WHAT WE CLAIM IS:—

1. A vulcanisable composition containing a major proportion of natural and/or synthetic rubber and a lesser proportion of isotactic polypropylene as hereinbefore defined.
2. A composition according to claim 1 having a content of the isotactic polypropylene between 1 and 40% by weight of the combined weight of rubber and the isotactic polypropylene.
3. A composition according to either of the preceding claims having a content of the isotactic polypropylene between 5 and 25% by weight of the combined weight of rubber and the isotactic polypropylene.
4. A composition according to any of the preceding claims in which the rubber is natural rubber and having a content of the isotactic polypropylene between 6 and 20% by weight of the combined weight of rubber and the isotactic polypropylene.
5. A composition according to any of the preceding claims having a content of the isotactic polypropylene between 1 and 20% by weight of the combined weight of rubber and the isotactic polypropylene.

preceding claims in which the isotactic polypropylene is at least 70% by weight insoluble in heptane.

5 6. A composition according to any of the preceding claims in which the isotactic polypropylene used has a melt viscosity at 190°C. less than 10⁷ poises.

10 7. A composition according to any of the preceding claims in which the isotactic polypropylene used has a melt viscosity at 190°C. between 10⁴ and 10⁵ poises.

8. A composition according to any of the preceding claims containing an antioxidant.

15 9. A process for the production of a composition according to any of the preceding claims in which the rubber and the isotactic polypropylene are masticated together at a temperature between 150°C. and the maximum of the isotactic polypropylene melting point range, the mixture obtained is cooled and vulcanising ingredients are dispersed in it by

mastication at a lower temperature.

10. A process according to claim 9 in which the polypropylene used is in the form of fine powder.

11. A process according to either of claims 9 or 10 in which antioxidant is incorporated in the composition when the rubber and isotactic polypropylene are initially masticated together.

12. Vulcanisable compositions substantially as hereinbefore described with particular reference to Example 1.

13. Vulcanisable compositions substantially as hereinbefore described in Examples 2 to 18.

14. A moulded article moulded from a vulcanisable composition claimed in any of claims 1 to 8 and 12 and 13.

WALTER SCOTT,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Vulcanisable Compositions

40 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

45 This invention relates to vulcanisable compositions.

Isotactic polypropylene is a crystalline material suitable for moulding and extrusion having a melting point of approximately 160° C. We have found that despite this high melting point it can be mixed with natural or synthetic rubber by a masticating process. We have also found that the presence of isotactic polypropylene in vulcanised natural or synthetic rubber compositions results in reinforcement to a remarkable extent.

According to the present invention, therefore, we provide vulcanisable compositions containing a major proportion of natural or synthetic rubber and a lesser proportion of isotactic polypropylene. We also provide a method for the production of these compositions in which method isotactic polypropylene is dispersed in the rubber by a hot masticating treatment in the absence of vulcanising ingredients and the mixture obtained is cooled and vulcanising ingredients are dispersed in it by mastication at a lower temperature.

Synthetic rubbers which may be used in this invention include copolymers of butadiene and styrene or acrylonitrile, copolymers of isoprene and isobutylene and polymers and copolymers of chloroprene.

Our preferred quantities of isotactic polypropylene in the compositions of this invention are between 1 and 40%, preferably between 5 and 25% by weight of the combined weight of rubber and isotactic polypropylene.

By isotactic polypropylene we mean any solid polymer of propylene which contains a major proportion of crystalline polypropylene and preferably is at least 70% insoluble in hot heptane. Also isotactic polypropylene may contain minor quantities as impurity of amorphous polypropylene, i.e. polypropylene having a random distribution of atoms along the greater part of its polymer chain and therefore not being crystallisable in itself. As a result, isotactic polypropylene normally melts over a range of temperatures.

We prefer that in the preparation of the compositions of this invention rubber is masticated with isotactic polypropylene in the absence of vulcanising ingredients at a temperature between 150°C. and the maximum of the polypropylene melting point range. For ease of dispersion, the polypropylene is preferably supplied for mastication in the form of fine powder. Mastication may be accomplished in, for example, a Banbury mixer or on open roll mills. In the former case, it is best to supply a dry blend of the ingredients to the mixer in order to minimise the mixing time and to complete the mixing on rolls in order to convert the mix to the form of sheet and thereby facilitate its cooling. If mastication is conducted on rolls only, the rubber may be sheeted on the rolls and powdered isotactic polypropylene added and milling continued until it is dispersed. Dispersion of the polypropylene in natural rubber is indicated by translucency in the mixture when hot.

This mastication of rubber and polypropylene is preferably conducted in the presence of an antioxidant. Suitable antioxidants are bis-(2 hydroxy-3-t-butyl-5-methyl phenyl) methane, a mixture of 2,4 and 2,5

- dimethyl phenol condensed with butyraldehyde and phenyl β naphthylamine. Suitable quantities of antioxidant are between 0.5% and 2.0% by weight of the composition.
- 5 Particularly suitable temperatures for masticating the rubber/polypropylene mix with vulcanising ingredients are between 60 and 80°C. for natural rubber and 25—35°C. for synthetic rubber. Again suitable equipment are Banbury mixers (preferably followed by open roll mills for sheeting) or open roll mills. Ancillary ingredients, for example, fillers and pigments, may usefully be added to the compositions together with the vulcanising ingredients.
- 10 Particularly valuable properties which are obtained when the compositions of our invention are vulcanised are those of tensile strength, modulus, high resilience, hardness, tear and abrasion resistance and electrical properties, with a remarkable retention of these good properties at elevated temperatures, all without the necessity of including dark coloured fillers. The compositions are accordingly particularly suitable for the production of light coloured articles of low heat build up, or light coloured articles in which a high degree of reinforcement is maintained at elevated temperatures or for use in applications
- 15 where a high tear strength and abrasion resistance is required. Fillers such as carbon black may be incorporated in the compositions for special applications.
- 20 The following example, in which all parts are by weight, serves to illustrate our invention. It will be understood, however, that our invention is in no way limited by this example.
- 35 **EXAMPLE**
160 gms. natural rubber were sheeted on a 12" x 6" open roll mill with 2 gms. bis-(2 hydroxy-3-t-butyl-5-methyl phenyl) methane at 155—160°C. and 40 gms. powdered polypropylene were added. This polypropylene had a melt viscosity at 190°C. of 5.6×10^4 poises measured on a parallel plate plastometer under a shear rate of 0.1 per second. When tested for solubility in heptane by Soxhlet extraction, 75% of it was found to be insoluble. 10 minutes after all the polypropylene had been added the sheet became translucent and was removed from the mill and cooled. The sheet obtained was fed to a 12" x 6" open roll mill heated to 60°C. and the following ingredients were added:
- 1.2 gms. Cyclohexyl benzthiazyl sulphen- amide 55
10.0 gms. Zinc oxide
4.0 gms. Stearic acid
5.0 gms. Sulphur
- The mixture was milled for 15 minutes during which time the temperature of the roll carrying the sheet was allowed to rise to 80°C. The sheet was cooled and test mouldings were moulded from it with a cure time of 30 minutes at 140°C. under a pressure of 1,000 lb./sq. inch. 60
- The properties of the mouldings were:
- Tensile strength 3,150 lb./sq. in.
Elongation at break 500%
Stress at 100% strain 990 lb./sq. in. 70
Stress at 300% strain 1,910 lb./sq. in.
- (The above tests were conducted according to B.S. 903 (1950) using ring specimens).
- Hardness, B.S. 903 (1950) 80 BS°
- 75 Crescent tear strength, B.S. 903 (1950) 1,2000 lb./sq. in.
- Resilience (Dunlop Tripsometer— B.S. 903 (1950)) at 20° C. 59%
at 50° C. 67%
at 70° C. 69%
- 80 Dynamic Young's Modulus at 0°C. 2.78×10^8 dynes cm²
at 30°C. 1.7×10^8 " "
at 60°C. 1.25×10^8 " "
at 80°C. 1.15×10^8 " "
at 100°C. 1.0×10^8 " "

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1959.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.